

WO 99/63955

PCT/FR99/01347

1

COSMETIC COMPOSITION COMPRISING AT LEAST ONE TACKY POLYMER
AND AT LEAST ONE FIXING POLYMER

The subject of the invention is a cosmetic
5 composition for keratinous fibres such as the hair
comprising, in a cosmetically acceptable medium, at least
one tacky polymer having a glass transition temperature of
less than 20°C and at least one fixing polymer having a
glass transition temperature greater than 15°C. It also
10 relates to a method of treating keratinous fibres such as
hair, in particular a method of fixing and/or maintaining
hairstyle, using the said composition as well as the use
of this composition in or for making a cosmetic
hairstyling formulation.

15 For the purposes of the present invention, the
expression "keratinous fibres" is understood to mean the
hair, the eyelashes and the eyebrows and the expression
"tacky polymer" a polymer which, after application by
pressing onto an identical polymer, resists an attempt at
20 separation.

The fixing of the hairstyle is an important
component of hairstyling which consists in maintaining the
shape already made or in shaping the hair and in fixing it
simultaneously. The expression "fixing polymer" is
25 understood to mean a polymer which maintains the shape of

the hair or which makes it possible to shape the hair and to fix it simultaneously.

The hair products for shaping and/or maintaining the hairstyle which are most common on the cosmetics market are compositions to be sprayed, essentially consisting of a solution, most often an alcohol or aqueous solution, and one or more materials, generally polymeric resins, whose function is to form bonds between the hair, also called fixing materials, in the form of a mixture with various cosmetic adjuvants. This solution is generally packaged either in an appropriate aerosol container pressurized with the aid of a propellant, or in a pump dispenser.

Hairstyling gels or foams are also known which are generally applied to wet hair before blow-drying or hair setting. Unlike conventional aerosol lacquers, these compositions have the disadvantage of not allowing the fixing of hair in a shape which already exists. Indeed, these compositions are essentially aqueous and their application wets the hair and cannot therefore maintain the initial shape of the hairstyle. To shape and fix the hairstyle, it is therefore necessary to then carry out blow-drying or drying.

Most of the compositions of the state of the art have the same disadvantage of not fixing or maintaining

the hairstyle for a sufficiently long period. Thus, the shape initially given to the hairstyle gradually disappears during the day, this in fact happening more quickly if the person is moving about. Consequently, it is often necessary to repeat all the hairstyling and fixing operations if it is desired to recover the initial hairstyle.

Hairstyling compositions are therefore being sought which offer a sufficiently strong fixing and maintaining effect for the hairstyle to suitably withstand the various stresses over time.

Finally, the compositions intended for fixing the hairstyle sometimes have the disadvantage of impairing the cosmetic properties of the hair. Thus, the hair may become rough, difficult to disentangle, lose its pleasant feel and appearance. Hairstyling compositions are therefore being sought which offer good cosmetic properties, in particular in terms of disentanglement, softness and feel.

A need therefore exists to find cosmetic compositions, in particular for hairstyling, which do not have the set of disadvantages indicated above.

Surprisingly and unexpectedly, the Applicant has discovered that when tacky polymers, in particular branched sulphonic polyesters or (meth)acrylic ester

polymers, are combined with certain fixing polymers, it is possible to obtain cosmetic compositions which meet the requirements expressed above.

The subject of the invention is therefore a
5 cosmetic composition for keratinous fibres such as the hair comprising, in a cosmetically acceptable medium, at least one tacky polymer having a glass transition temperature (T_g) of less than 20°C and at least one fixing polymer having a glass transition temperature (T_g) greater
10 than 15°C .

Advantageously, a tacky polymer is chosen which has a peeling profile defined by at least one maximum peeling force $F_{\max} > 3$ Newton, and preferably greater than 5 N.

15 More advantageously still, the peeling profile is defined, in addition, by an energy for separation $E_s(M/V)$ of the material brought into contact with a glass surface of less than $300 \mu\text{J}$, when the glass transition temperature of the tacky polymer is less than -15°C .

20 The maximum peeling force F_{\max} is the maximum tensile force, measured with the aid of an extensometer, necessary to peel apart the respective 38 mm^2 surfaces of two rigid, inert and nonabsorbent supports (A) and (B) placed opposite each other; the said surfaces being
25 previously coated with the tacky polymer previously

dissolved at 5% in an aqueous, aqueous-alcoholic or alcoholic solvent, at the rate of 1 mg/mm², dried for 24 hours at 22°C under a relative humidity of 50%, then subjected for 20 seconds to a compression of 3 Newton and finally subjected for 30 seconds to pulling at the rate of 20 mm/min.

Advantageously, supports (A) and (B) consisting of polyethylene, polypropylene, metal alloy or glass are used.

10 The separation energy $E_{s(M/V)}$ is the energy provided by the extensometer in order to carry out the separation of the respective 38/mm² surfaces of two rigid, inert and nonabsorbent supports (C) and (D) placed opposite each other; one of the said supports consisting
15 of cut glass and the other of the said supports being of an identical nature to the supports (A) and (B) as defined in Claim 4 or 5 and whose surface is previously coated with the tacky polymer previously dissolved at 5% in an aqueous, aqueous-alcoholic or alcoholic solvent, at the
20 rate of 1 mg/mm², dried for 24 hours at 22°C under a relative humidity of 50%, the two surfaces of the said supports (C) and (D) being subjected for 20 seconds to a compression of 3 Newton and finally subjected for 30 seconds to pulling at the rate of 20 mm/min.

The separation energy $E_{s(M/V)}$ is work which can be calculated by means of the following formula:

$$\int_{x_{s1}+0.05}^{x_{s2}} F(x) dx$$

where $F(x)$ is the force necessary to produce a

5 movement(x);

x_{s1} is the movement (expressed in millimetres) produced by the maximum tensile force;

x_{s2} is the movement (expressed in millimetres) produced by the tensile force which allows the complete separation of
10 the two surfaces of the supports (C) and (D).

Preferably, a tacky polymer will be chosen such that the maximum peeling force F_{max} is greater than 5 Newton and/or such that its glass transition temperature (T_g) is less than 20°C. If the T_g of the polymer is less
15 than -15°C, it will preferably need to have in addition a separation energy $E_{s(M/V)}$ of less than 300 μJ .

The relative concentration by weight of tacky polymer in the composition is in general greater than 0.01%, more preferably greater than 0.1%, and more
20 preferably still greater than 0.5%.

According to a first advantageous embodiment of the present invention, a branched sulphonic polymer or (meth)acrylic ester polymers are chosen as tacky polymer.

Advantageously, a fixing polymer is chosen which
25 has a glass transition temperature (T_g) greater than 25°C.

In accordance with the invention, the relative concentration by weight of fixing polymer in the composition is in general greater than 0.01%, and preferably greater than 0.1%.

- 5 A particularly preferred form of the branched sulphonic polyester is that obtained by polymerization of:
- (i) at least one difunctional dicarboxylic acid not carrying a sulphonic function;
 - (ii) at least one difunctional monomer carrying at
10 least one sulphonic function, the functional group(s) being chosen from the group comprising hydroxyl, carboxyl and amino groups; /
 - (iii) at least one diol or a mixture of diol(s) and of diamine(s);
 - 15 (iv) optionally one difunctional monomer chosen from the group comprising hydroxycarboxylic acids, aminocarboxylic acids and mixtures thereof;
 - (v) at least one multifunctional reagent carrying at least three functional groups chosen from the group
20 comprising amino, alcohol and carboxylic acid groups.

Such a polymerization may be carried out starting with:

- (i) at least one difunctional dicarboxylic acid not carrying a sulphonic function;

- (ii) 2 to 15 relative mol% of difunctional monomer carrying at least one sulphonic function;
- (iii) at least one diol or a mixture of diol(s) and of diamine(s);
- 5 (iv) 0 to 40 relative mol% of the difunctional monomer chosen from the group comprising the hydroxycarboxylic acids, the aminocarboxylic acids and mixtures thereof;
- 10 (v) 0.1 to 40 relative mol% of the multifunctional reagent carrying at least three reactive functional groups.

The branched sulphonic polymers preferably contain substantially equal proportions, as number of equivalents, of carboxylic acid functions, on the one
 15 hand, and of diol and/or diol and diamine functions, on the other hand.

The difunctional dicarboxylic acid (i) is preferably chosen from the group comprising aliphatic dicarboxylic acids, alicyclic dicarboxylic acids, aromatic
 20 dicarboxylic acids or a mixture thereof and more particularly from the group comprising 1,4-cyclohexanedioic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, fumaric acid, maleic acid, 1,3-cyclohexanedioic acid, phthalic acid,

terephthalic acid and isophthalic acid or mixtures thereof.

The difunctional monomer (ii) as defined above is preferably chosen from the group comprising
5 dicarboxylic acids, dicarboxylic acid esters, glycols and hydroxy acids each containing at least one metal sulphonate group.

The diol (iii) is preferably chosen from the group comprising alkanediols and polyalkylenediols and
10 more particularly from the group comprising ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol and polypropylene glycol.

The diamine (iii) may be chosen from the group comprising alkanediamines and polyalkylenediamines.

15 The multifunctional reagent (v) is preferably chosen from the group comprising trimethylolethane, trimethylolpropane, glycerol, pentaerythritol, sorbitol, trimellitic anhydride, erythritol, threitol, dipentaerythritol, pyromellitic dianhydride and
20 dimethylpropionic acid.

The branched sulphonic polymers more particularly desired by the present invention are those described in patent applications WO 95/18191, WO 97/08261 and WO 97/20899.

In accordance with the invention, there is advantageously chosen, as branched sulphonic polymer, the polymer AQ 1350 marketed by the company Eastman. This polymer AQ 1350 is defined by:

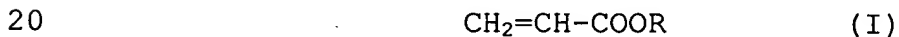
- 5 - a glass transition temperature, given by the supplier, equal to 0°C;
- a maximum peeling force F_{\max} equal to 25 N.

According to a second advantageous embodiment of the compositions in accordance with the invention, a
10 (meth)acrylic ester polymer is used as tacky polymer.

The tacky (meth)acrylic ester polymers used in accordance with the invention advantageously comprise:

- (a) from 9 to 99% by weight of a (meth)acrylic ester monomer relative to the total weight of the polymer;
- 15 (b) up to 90% of comonomer(s);
- (c) from 1 to 10% of a vinylidene monomer containing a carboxyl or hydroxyl group.

The (meth)acrylic ester monomer (a) generally corresponds to the formula (I) or (II):

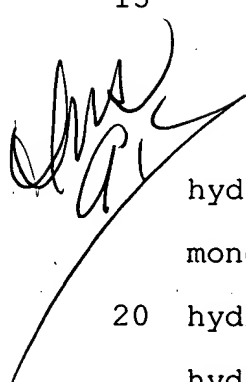


in which R represents a C_1 to C_{18} alkyl, an alkoxy(C_2 to C_8 alkyl), an alkylthio(C_2 to C_8 alkyl) or a C_2 to C_8 cyanoalkyl. By way of example, the monomer (a) may be
25 chosen from the group comprising methyl acrylate, ethyl

acrylate, n-butyl acrylate, isobutyl acrylate, hexyl acrylate, octyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, methoxyacrylate, ethoxyacrylate, methylthiomethyl acrylate and cyanopropyl acrylate.

5 The comonomer (b) may contain one or more vinylidene groups having terminal $\text{CH}_2=\text{C}$ groups, such as:

- acrylic or methacrylic esters, such as methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, methyl ethacrylate,
- 10 - vinyl halides such as vinyl chloride;
- vinyl and allyl esters such as vinyl acetate, vinyl butyrate, vinyl chloroacetate;
- aromatic vinyls such as styrene, vinyltoluene, chloromethylstyrene, vinylnaphthalene; and
- 15 - vinyl nitriles such as acrylonitrile or methacrylonitrile.

 Among the vinylidene monomers containing hydroxyl groups (c), there may be mentioned acrylate monomers containing a terminal hydroxyl group, such as

20 hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, hydroxybutyl acrylate or alternatively certain hydroxymethylated derivatives of diacetone acrylamide, for example N-methylolacrylamide, N-methylolmaleamide,

~~N-propanolacrylamide, N-methylolmethacrylamide,
N-methylol p-vinylbenzamide.~~

Among the vinylidene monomers containing carboxyl groups (c), there may be mentioned for example
5 acrylic or methacrylic acid, itaconic acid, citraconic acid, maleic acid.

The tacky (meth)acrylic ester polymers particularly desired by the present invention are those described in patents US 5 234 627 and US 4 007 147.

10 In accordance with the invention, the polymer Hycar 26 120 marketed by the company Goodrich is advantageously chosen as (meth)acrylic ester polymers. This polymer Hycar 26 120 is defined by:

- 15 - a glass transition temperature, given by the supplier, equal to -10°C ;
- a maximum peeling force F_{max} equal to 6.25 N.

The fixing polymer is generally chosen from anionic, cationic, amphoteric and nonionic fixing polymers and mixtures thereof.

20 These fixing polymers may be used in solubilized form or alternatively in the form of a dispersion of solid particles of polymer.

As cationic fixing polymer, there is preferably chosen the polymers comprising primary, secondary,
25 tertiary and/or quaternary amine groups which are part of

the polymer chain or which are directly attached to it, and having a molecular weight of between 500 and about 5,000,000 and preferably between 1000 and 3,000,000.

As anionic fixing polymers, there are preferred
5 the polymers comprising groups derived from a carboxylic, sulphonic or phosphoric acid and which have a weight-average molecular weight of between about 500 and 5,000,000.

As amphoteric fixing polymers, there are
10 preferably chosen the polymers comprising B and C units randomly distributed in the polymer chain, where B denotes a unit derived from a monomer comprising at least one basic function, in particular a basic nitrogen atom and C denotes a unit derived from an acidic monomer comprising
15 one or more carboxylic or sulphonic groups or alternatively B and C may denote groups derived from zwitterionic monomers of carboxybetaines or sulphobetaines; B and C may also denote a cationic polymer chain comprising primary, secondary, tertiary or
20 quaternary amine groups, in which at least one of the amine groups carries a carboxylic or sulphonic group attached via a hydrocarbon radical; or alternatively B and C are part of a chain of a polymer containing an ethylene- α,β -dicarboxylic unit of which one of the carboxylic

groups has been caused to react with a polyamine comprising one or more primary or secondary amine groups.

As nonionic fixing polymers, polyurethanes are advantageously chosen.

5 Among the fixing polymers used in solubilized form, the polymers chosen from the group comprising silicone-containing acrylic polymers, polymers based on a vinylpyrrolidone and vinylcaprolactam monomer will be preferably used.

10 Among the fixing polymers which exist in the form of a dispersion, those comprising acrylic or methacrylic monomers and esters thereof or alternatively those comprising styrene monomers will be preferably used.

 The composition may be provided in vaporizable,
15 foam, gel or lotion form and the cosmetically acceptable vehicle may consist of an appropriate solvent to which additives such as gelling agents or foaming agents are added. In general, the solvent is chosen from water, alcohols or an aqueous-alcoholic mixture.

20 The compositions may contain, in addition, an appropriate quantity of propellants such as customary compressed or liquefied gases, preferably compressed air, carbon dioxide or nitrogen, or alternatively a gas which is soluble or otherwise in the composition, such as

dimethyl ether, hydrocarbons which are fluorinated or otherwise and mixtures thereof.

The subject of the invention is also an aerosol device consisting of a container containing an aerosol composition consisting, on the one hand, of a liquid phase (or juice) containing at least one composition in accordance with the invention in an appropriate solvent and a propellant as well as a means of distributing the said aerosol composition.

Yet another subject of the invention is a method of treating keratinous fibres, in particular hair, characterized in that the composition in accordance with the invention is applied to the said fibres before or after shaping the hairstyle.

The composition in accordance with the invention is generally used in or for making a cosmetic hairstyling formulation.

The examples below make it possible to illustrate the invention without however seeking to limit the scope thereof. The polymers indicated below will be used:

Amphomer	Octylacrylamide/acrylate/butyl-aminoethyl/methacrylate copolymer marketed by National Starch
----------	--

Polymer LO-21 DRY	Polydimethyl/methyl siloxane containing methyl 3-propylthio- acrylate/methyl methacrylate/ methacrylic acid groups marketed by 3M
Luviskol VA64P	Polyvinylpyrrolidone marketed by BASF
Uramul SC 132	Acrylic copolymer latex marketed by DMS RESINS; $T_g = 50^\circ\text{C}$
AQ 1350	Branched sulphonic polyester marketed by the company Eastman

EXAMPLES:

Compositions in accordance with the invention comprising a combination of a branched sulphonic polymer and a fixing polymer are compared below with compositions in accordance with the prior art containing either the branched sulphonic polymer alone, or the fixing polymer alone.

Example 1 (comparative):

Sensory tests are carried out in order to compare the performance of compositions in accordance with the invention and of compositions in accordance with the prior art. The comparison is made on the retention of the hairstyle over time and under a constraint.

For that, 3 compositions in accordance with the invention and 4 compositions in accordance with the prior art are made. These compositions are applied to wigs of natural hair. Next, the shape retention of the wig and the return of the shape of the wigs after shaking are evaluated.

Composition 1 (invention):

AQ 1350	4 g
Amphomer	2 g
Water	75 g
2-Amino-2-methyl-1-propanol qs	0.37 g
neutralization Amphomer	
Alcohol qs	100 g

Composition 2 (invention):

AQ 1350	4 g
Polymer LO-21 DRY previously 90%	2 g

neutralized

Water		75 g
Alcohol	qs	100 g

Composition 3 (invention):

AQ 1350		4 g
LUVISKOL VA 64 P		2 g
Water		75 g
Alcohol	qs	100 g

Composition 4 (prior art - branched sulphonic polyester alone):

AQ 1350		6 g
Water		75 g
Alcohol	qs	100 g

Composition 5 (prior art - fixing polymer alone):

Amphomer		6 g
Water		75 g
2-Amino-2-methyl-1-propanol	qs	1.09 g

neutralization Amphomer

Alcohol	qs	100 g
---------	----	-------

Composition 6 (prior art - fixing polymer alone):

Polymer LO-21 DRY previously 90%	6 g
----------------------------------	-----

neutralized

Water	75 g
-------	------

Alcohol	qs	100 g
---------	----	-------

Composition 7 (prior art - fixing polymer alone):

LUVISKOL VA 64 P	6 g
------------------	-----

Water	75 g
-------	------

Alcohol	qs	100 g
---------	----	-------

Each of the compositions is introduced into a pump dispenser. 3 grams of each composition are sprayed onto a wig of hair 20 cm long previously shampooed and drained. It is allowed to dry for 4 hours and the wig is turned over.

The wig is shaken by means of an alternating rotation for 2 hours. The final shape of the locks is compared with the shape which they had before shaking and

the shape retention is estimated. A score from 0 to 5 is used:

- 0 indicates a very poor shape retention and a completely collapsed hairstyle,
- 5 - 5 indicates an excellent retention and a hairstyle which has remained intact and voluminous in spite of the shaking.

The wigs are then disentangled and they are again shaken for 20 seconds. The return of the shape of the hairstyle when it has been subjected to all these operations is estimated. The same score scale ranging from 0 to 5 is used.

Table 1 summarizes the results.

Table 1

Composition	Shape retention after shaking	Return of the shape after shaking and disentanglement
1	3.25	2.5
2	4.0	4.0
3	4.5	4.25
4	2.0	4.0
5	3.75	0.75
6	3.5	1.0
7	2.0	0.75

without treatment	0	0.5
-------------------	---	-----

Table 1 shows that the compositions in accordance with the invention and comprising the combination of polymers offer better results in terms of shape retention after shaking and of a return of the shape after shaking and disentanglement than the compositions in accordance with the prior art.

10

Example 2:

A composition 8 in accordance with the invention is prepared and the retention of the hairstyle as well as certain cosmetic properties are estimated.

15

Composition 8 (invention):

AQ 1350	4 g
URAMUL SC 132	0.5 g
Water qs	100 g

A wig of 20 g of natural hair is taken and 2.5 grams of composition 8 are applied to the hair and allowed to dry.

It is observed that the hair is maintained very well. Disentanglement is easy and the locks have a good feel after disentanglement.